Lecture 5 - Constitutive Equations

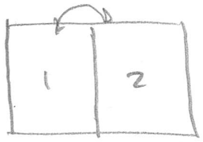
I. What are the transport phenomena?

* You learned in thermodynamics that systems with different temperatures evolve to the same temperature when brought in contact. Similarly, pressures & chemical potentials approach one another:

$T_1 = T_2$ thermal equilibrium

$P_1 = P_2$ mechanical equilibrium

$\mu_1 = \mu_2$ chemical equilibrium



motion of mass, momentum, energy

* If we think about this in a single system (shrink 1 & 2) we want $\nabla T \to 0$, $\nabla P \to 0$ & $\nabla \mu \to 0$.

* In Transport phenomena, we want to know how systems move towards equilibrium. How do temperatures, pressures, and species distribute in space & time,

* This is very practical, because systems are rarely (never?) in equilibrium. It is also a bit complicated because we need partial differential equations (PDEs) to describe this process. We are going to derive & begin to understand these equations in the next several lectures.

* Gradients of T, P, & μ_i are like forces that move something around in space & time. They move energy, momentum, & mass fluxes respectively.

Forces	Fluxes	Transport
T	u	Energy
P	V	Displacement/ Momentum
(*) $\underline{\underline{\sigma}}$	$\underline{\underline{\varepsilon}}$, $\nabla \underline{v}$	
μ_i	n_i	Species mass

(*) PV is a bit funky (1D only). Momentum in 3D has a stress, $\underline{\underline{\sigma}}$, strain $\underline{\underline{\varepsilon}}$, and a rate of strain, $\nabla \underline{v}$

(**) These columns are thermodynamic conjugates:

$$ds = \frac{1}{T}du + \frac{P}{T}dV - \sum_{i=1}^{N} \frac{\mu_i}{T} dn_i$$

* In order to get our transport equations, we will need two things.

(1) Balance Equations: Energy, momentum, and mass are conserved quantities. We can write conservation laws (think about a "bank account") as PDEs.

(2) Constitutive Laws: Balance equations only tell us what is conserved. We need some way to relate how much flux of energy, mass, & momentum comes when we have a "force" due to T, P ($\underline{\underline{\sigma}}$), or μ.

$\nabla T \rightarrow$ flux of energy?

∇P or $\nabla \cdot \underline{\underline{\sigma}} \rightarrow$ flux of momentum?

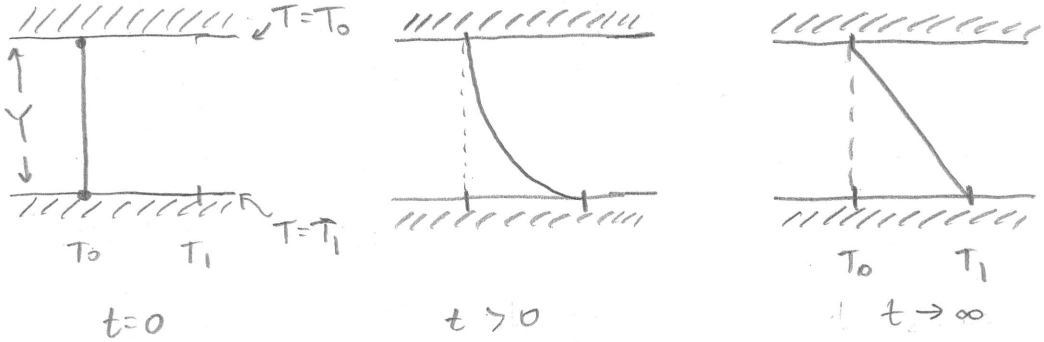
$\nabla \mu_i \rightarrow$ flux of mass of i?

- Constitutive laws are not "first principles." They are based on observations.
- They are affected by the material properties of the medium
- "Fourier's Law", "Fick's Law", "Newton's law of viscosity"

{Aside} Chemical kinetics is not one of our transport phenomena. Why? Chemical affinity, $A = \sum_i \nu_i \mu_i$ is a force with a flux, ξ, extent of reaction. However, ξ is not a conserved quantity. Also, there are no constitutive laws relating $\nabla \xi$ to A, driving kinetics. As such, chemical kinetics is in a different class of "relaxation" processes.

II. 1D constitutive laws

* Consider the following thought experiment: two parallel plates of aluminum with polythylene between:



Y: gap between plates A: plate area

- Everything is T=T₀ before t=0. Then swith the bottom plate to T=T₁ at t=0. How does energy move?
- Repeated observations show that at t→∞:

$$\frac{\dot{Q}}{A} \propto \frac{T_0 - T_1}{Y}$$

- negative b/c heat moves "down" the gradient. convention

$$\frac{\text{heat energy}}{\text{area} \times \text{time}} \propto \text{temperature gradient}$$

"thermal conductivity"

$$\frac{\dot{Q}}{A} = -k \frac{\Delta T}{Y} \Rightarrow \boxed{q_y = -k \frac{dT}{dy}}$$

material-dependent constant of proportionality

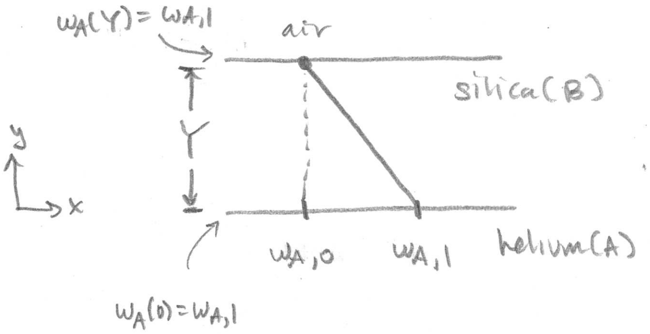
flux in y-dir

"force"

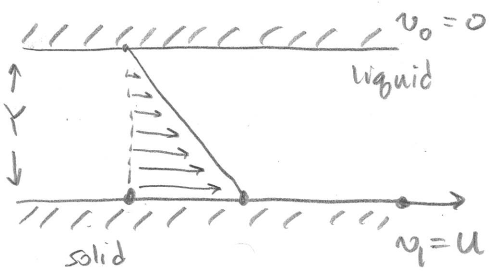
- This is called "Fourier's law of conduction". It is a constitutive law.

* This thought experiment is not unique to energy (heat) transfer

mass trasfer



Momentum transfer



$$\frac{\dot{w}_{A,y}}{A} = \rho D_{AB} \frac{w_{A,0} - w_{A,1}}{Y}$$

mass / area × time; density; binary diffusivity; mass fraction gradient

$$\frac{F}{A} = \mu \frac{U}{Y}$$

viscosity; stress or momentum / area × time; velocity gradient

- Notice sign difference!

$$\boxed{j_{A,y} = -\rho D_{AB} \frac{dw_A}{dy}}$$

Fick's law of diffusion

$$\boxed{\tau_{yx} = \mu \frac{dv_x}{dy}}$$

Newton's law of viscosity

* Some notes:

- what about chemical potential? $\frac{d\mu_A}{dy} = \frac{d\mu_A}{dw_A} \cdot \frac{dw_A}{dy}$ ← chain rule

↳ get $d\mu_A / dw_A$ from thermo:

$$\mu_A = \mu_A^* + RT \ln(\gamma_A x_A)$$

$$\frac{d\mu_A}{dw_A} = RT \frac{\partial}{\partial w_A}\left[\ln(\gamma_A x_A)\right]$$

μ_A^* : pure species chem pot
γ_A : activity coeff
x_A : mole fraction

- What is τ_{yx}? shear stress : y - unit normal of stress surface, x - force component

momentum flux tensor : y - unit normal of direction of transport
x - momentum component

τ_{yx}: y → D: Surface Direction; x → C: force/momentum Component

III. 3D constitutive laws

- Hopefully you've seen the above before. They are the "undergrad" version. we want to be able to do this in 3D in arbitrary coordinates. Maybe the materials are complex. Need "grad school" version.

- Quick note: These fluxes are the "diffusive" fluxes only. we will see later that there are also "convective" fluxes. Put a pin in that. Don't worry if that doesn't mean anything to you yet.

A. Energy Flux

- In 3D, Fourier's law becomes:

$$\underline{q} = -k\,\underline{\nabla} T$$

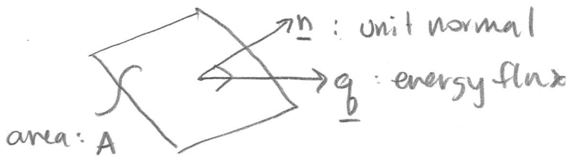
↖ flux is a vector

- If the material is anisotropic, we need a conductivity tensor:

$$\underline{q} = -\underline{\underline{k}} \cdot \underline{\nabla} T$$

$\underline{\underline{k}}$: 3x3 matrix of conductivities

- Flux through an arbitrary surface?



rate of heat/energy transfer : $(\underline{n}\cdot\underline{q})A = -k(n\cdot\underline{\nabla} T)A$

B. Species Mass Flux

- In 3D, Fick's law becomes:

$$\underline{j}_A = -\rho D_{AB} \underline{\nabla} w_A \qquad \underset{\substack{\uparrow\\ \text{total}\\ \text{density}}}{\rho} = \sum_i \underset{\substack{\uparrow\\ \text{species}\\ \text{density}}}{\rho_i} \qquad \underset{\substack{\uparrow\\ \text{mass fraction}}}{w_i} = \frac{\rho_i}{\rho}$$

* It is sometimes convenient to use a molar flux:

$$\underline{J}_A^{(M)} = -c D_{AB} \nabla x_A \qquad \underset{\substack{\uparrow\\ \text{total}\\ \text{Concentation}}}{c} = \sum_i \underset{\substack{\uparrow\\ \text{species}\\ \text{conc.}}}{c_i} \qquad \underset{\substack{\uparrow\\ \text{mole}\\ \text{fraction}}}{x_i} = \frac{c_i}{c}$$

* Both of these fluxes are defined so they obey the property:

$$\sum_i \underline{j}_i = \underline{0} \quad \& \quad \sum_i \underline{J}_i^{(M)} = \underline{0}$$

This is done using different velocity averages (mass-averaged, molar-averaged). You will get practice converting between the two forms on your HW.

C. Momentum Flux

* In 3D, Newton's law of viscosity is:

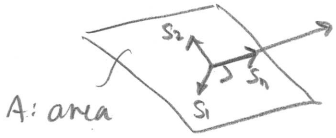
$$\underset{\substack{\uparrow\\ \text{momentum}\\ \text{flux or}\\ \text{viscous}\\ \text{stress}}}{\underline{\underline{\tau}}} = \underset{\substack{\uparrow\\ \text{viscosity}}}{\mu} \underbrace{\left[(\nabla \underline{v}) + (\nabla \underline{v})^T\right]}_{\substack{\text{rate-of-stain}\\ \text{tensor}}} = 2\mu \underline{\underline{\Gamma}}$$

$$\underline{\underline{\Gamma}} = \frac{1}{2}\left[(\nabla \underline{v}) + (\nabla \underline{v})^T\right]$$

(symmetric tensor)

* This is for a Newtonian fluid. Remember, constitutive laws depend on the material. The field of rheology is dedicated to the study of constitutive laws of non-Newtonian fluids.

* Flux of momentum through an arbitrary surface?



$\underline{n}$: surface unit normal

$\underline{S}(\underline{n})$: stress vector (force/area)
(momentum vector)

$$s(n) = \underline{n}\cdot\underline{\underline{\tau}} \longrightarrow \text{momentum rate} = (\underline{n}\cdot\underline{\underline{\tau}})\,A$$

$$\underset{\substack{\uparrow\\ \text{direction}\\ \text{(of unit normal)}}}{\tau_i}\,{}_{j}\ \nwarrow \text{component (of momentum / stress)}$$

"remember : DC"

* stress & momentum flux really do have the same units :

$$\text{stress} = \frac{\text{force}}{\text{area}} = \frac{\text{kg m}}{s^2}\,\frac{1}{m^2} = \frac{\text{kg}}{m s^2} \quad ✓$$

$$\text{force} = \frac{\text{momentum}}{\text{time}} \quad \left(\text{Newton's } 2^{nd} \text{ law } F = \frac{dp}{dt}\right)$$

$$\frac{\text{momentum}}{\text{area}\cdot\text{time}} = \frac{\text{kg m}}{s}\cdot\frac{1}{m^2}\,\frac{1}{s} = \frac{\text{kg}}{m s^2} \quad ✓$$